

# Thermodynamic guidelines for the prediction of hydrogen storage reactions and their application to destabilized hydride mixtures

Donald J. Siegel,<sup>1</sup> C. Wolverton,<sup>1,\*</sup> and V. Ozoliņš<sup>2</sup>

<sup>1</sup>Ford Motor Company, MD1170/RIC, Dearborn, MI 48121

<sup>2</sup>Department of Materials Science and Engineering, University of California, Los Angeles, CA 90095

(Dated: February 2, 2008)

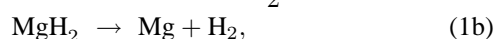
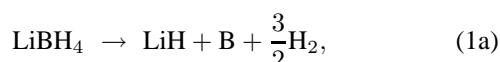
We propose a set of thermodynamic guidelines aimed at facilitating more robust screening of hydrogen storage reactions. The utility of the guidelines is illustrated by reassessing the validity of reactions recently proposed in the literature, and through vetting a list of more than 20 candidate reactions based on destabilized  $\text{LiBH}_4$  and  $\text{Ca}(\text{BH}_4)_2$  borohydrides. Our analysis reveals several new reactions having both favorable thermodynamics and relatively high hydrogen densities (ranging from 5-9 wt.%  $\text{H}_2$  & 85-100 g  $\text{H}_2/\text{L}$ ), and demonstrates that chemical intuition alone is not sufficient to identify valid reaction pathways.

## I. INTRODUCTION

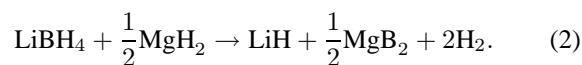
The potential of emerging technologies such as fuel cells (FCs) and photovoltaics for environmentally-benign power generation has sparked renewed interest in the development of novel materials for high-density energy storage. For mobile applications such as in the transportation sector, the demands placed upon energy storage media are especially stringent,<sup>1</sup> as the leading candidates to replace fossil-fuel-powered internal combustion engines (ICEs)—proton exchange membrane FCs and hydrogen-powered ICEs ( $\text{H}_2$ -ICEs)—rely on  $\text{H}_2$  as a fuel. Although  $\text{H}_2$  has about three times the energy density of gasoline by weight, its volumetric density, even when pressurized to 10,000 psi, is roughly six times less than that of gasoline. Consequently, safe and efficient storage of  $\text{H}_2$  has been identified<sup>2</sup> as one of the key scientific obstacles to realizing a transition to  $\text{H}_2$ -powered vehicles.

Perhaps the most promising approach to achieving the high  $\text{H}_2$  densities needed for mobile applications is via absorption in solids.<sup>3</sup> Metal hydrides such as  $\text{LaNi}_5\text{H}_6$  have long been known to reversibly store hydrogen at volumetric densities surpassing that of liquid  $\text{H}_2$ , but their considerable weight results in gravimetric densities that are too low for lightweight applications.<sup>4</sup> Accordingly, recent efforts<sup>5,6,7,8,9</sup> have increasingly focused on low-Z complex hydrides, such as metal borohydrides,  $M(\text{BH}_4)_n$ , where  $M$  represents a metallic cation, as borohydrides have the potential to store large quantities of hydrogen (up to 18.5 wt.% in  $\text{LiBH}_4$ ). Nevertheless, the thermodynamics of  $\text{H}_2$ -desorption from known borohydrides are generally not compatible with the temperature-pressure conditions of FC operation: for example, in  $\text{LiBH}_4$  strong hydrogen-host bonds result in desorption temperatures in excess of 300°C.<sup>6</sup> Thus the suitability of  $\text{LiBH}_4$  and other stable hydrides as practical  $\text{H}_2$ -storage media will depend upon the development of effective destabilization schemes.

Building on earlier work by Reilly and Wiswall,<sup>10</sup> Vajo *et al.*<sup>11</sup> recently demonstrated that  $\text{LiBH}_4$  can be destabilized by mixing with  $\text{MgH}_2$ . In isolation, the decomposition of these compounds proceeds according to:



yielding 13.6 and 7.6 wt.%  $\text{H}_2$ , respectively, at temperatures above 300°C. The high desorption temperatures are consistent with the relatively high enthalpies of desorption:  $\Delta H \sim 67$  ( $\text{LiBH}_4$ ) and  $\sim 70$  ( $\text{MgH}_2$ ) kJ/(mol  $\text{H}_2$ ).<sup>11,12</sup> By mixing  $\text{LiBH}_4$  with  $\text{MgH}_2$ ,  $\Delta H$  for the combined reaction can be decreased below those of the isolated compounds due to the exothermic formation enthalpy of  $\text{MgB}_2$ :



That is, formation of the  $\text{MgB}_2$  product *stabilizes* the dehydrogenated state in Eq. 2 relative to that of Eq. 1, thereby *destabilizing* both  $\text{LiBH}_4$  and  $\text{MgH}_2$ . By adopting this strategy, measured isotherms for the  $\text{LiBH}_4 + \frac{1}{2}\text{MgH}_2$  mixture over 315–400°C exhibited a 25 kJ/mol  $\text{H}_2$  decrease in  $\Delta H$  relative to  $\text{LiBH}_4$  alone, with an approximately tenfold increase in equilibrium  $\text{H}_2$  pressure.<sup>11</sup> In addition, the hydride mixture was shown to be reversible with a density of 8–10 wt.%  $\text{H}_2$ .<sup>11</sup> Nevertheless, the extrapolated temperature of  $T = 225^\circ\text{C}$  at which  $P_{\text{H}_2} = 1$  bar is still too high for mobile applications, and suggests that *additional* destabilization is necessary.

The concept of thermodynamic destabilization appears to offer new opportunities for accessing the high  $\text{H}_2$  content of strongly-bound hydrides. However, the large number of known hydrides suggests that experimentally testing all possible combinations of known compounds would be impractical; thus a means for rapidly screening for high-density  $\text{H}_2$ -storage reactions with appropriate thermodynamics<sup>13</sup> would be of great value.<sup>33</sup> Towards these ends, here we employ first-principles calculations to identify new  $\text{H}_2$ -storage reactions with favorable temperature-pressure characteristics based on destabilizing  $\text{LiBH}_4$  and  $\text{Ca}(\text{BH}_4)_2$ <sup>9</sup> by mixing with selected metal hydrides. Our goal is to determine whether additional destabilization of  $\text{LiBH}_4$  and  $\text{Ca}(\text{BH}_4)_2$ —beyond that demonstrated<sup>11</sup> with  $\text{LiBH}_4/\text{MgH}_2$ —is possible by exploiting the exothermic formation enthalpies of the metal borides. We focus specifically on thermodynamic issues since appropriate thermodynamics is a necessary condition for any viable storage material, and thermodynamic properties are not easily altered. While kinetics must also be considered, catalysts and novel synthesis routes have been shown to be effective at improving reversibility and the rates of  $\text{H}_2$  uptake/release.<sup>14</sup> By screening through  $\sim 20$  distinct reactions, we identify four

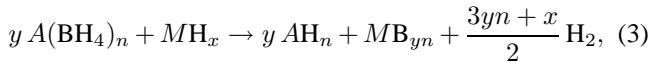
new destabilized mixtures having favorable Gibbs free energies of desorption in conjunction with high gravimetric (5–9 wt.%) and volumetric (85–100 g H<sub>2</sub>/L) storage densities. The predicted reactions present new avenues for experimental investigation, and illustrate that compounds with low gravimetric densities (i.e., transition metal hydrides) may yield viable H<sub>2</sub>-storage solutions when mixed with lightweight borohydrides. An advantage of the present approach is that it relies only on known compounds with established synthesis routes, in contrast to other recent studies which have proposed H<sub>2</sub>-storage reactions based on materials which have yet to be synthesized.<sup>15,16,17,18,19</sup>

An additional distinguishing feature of this study is the development of a set of thermodynamic guidelines aimed at facilitating more robust predictions of hydrogen storage reactions. The guidelines are used to vet the present set of candidate reactions, and to illustrate how other reactions recently reported in the literature<sup>13</sup> are thermodynamically unrealistic. In total, this exercise reveals some of the common pitfalls that may arise when attempting to simply “guess” at reaction mechanisms.

## II. METHODOLOGY

Our first-principles calculations were performed using a planewave-projector augmented wave method (VASP)<sup>20,21</sup> based on the generalized gradient approximation<sup>22</sup> to density functional theory. All calculations employed a planewave cut-off energy of 400 eV, and k-point sampling was performed on a dense grid with an energy convergence of better than 1 meV per supercell. Internal atomic positions and external cell shape/volume were optimized to a tolerance of better than 0.01 eV/Å. Thermodynamic functions were evaluated within the harmonic approximation,<sup>23</sup> and normal-mode vibrational frequencies were evaluated using the so-called direct method on expanded supercells.<sup>24,25,26,27</sup> Further information regarding the details and experimental validation of our calculations can be found elsewhere.<sup>25,26,27</sup>

Our search for high-density H<sub>2</sub>-storage reactions is based on a series of candidate reactions that are analogous to Eq. 2:



where  $A = \text{Li}$  or  $\text{Ca}$  [ $n = 1$  (2) for  $\text{Li}$  ( $\text{Ca}$ )],  $M$  represents a metallic element, and the coefficients  $x$  and  $y$  are selected based on the stoichiometries of known hydrides  $M\text{H}_x$  and borides  $M\text{B}_{yn}$ . To maximize gravimetric density we limit  $M$  to relatively light-weight elements near the top of the periodic table. In the case of  $A = \text{Li}$ , the enthalpy of Eq. 3 per mol H<sub>2</sub> can be expressed as:

$$\Delta H = \frac{2}{3y+x} \left[ \frac{3y}{2} \Delta H^{\text{LiBH}_4} + \frac{x}{2} \Delta H^{M\text{H}_x} - \Delta H^{M\text{B}_y} \right] \quad (4)$$

where  $\Delta H^i$  are the desorption (formation) enthalpies of the respective hydrides (borides) per mol H<sub>2</sub> ( $M$ ). Thus  $\Delta H$  for the destabilized LiBH<sub>4</sub> reaction is simply an average of the

hydride desorption enthalpies, less the enthalpy of boride formation.

## III. RESULTS

Table I lists theoretical H<sub>2</sub> densities, and calculated dehydrogenation enthalpies and entropies for several potential H<sub>2</sub>-storage reactions. Reactions 1–22 enumerate the candidate new reactions, while reactions 23–27 are included in order to validate the accuracy of our predictions by comparing with experimentally-measured enthalpies<sup>11,12,29</sup> and previous first-principles results<sup>13</sup> (shown in parentheses). Turning first to the reactions from experiment (24–27), it is clear that the calculated  $T = 300$  K enthalpies are generally in good agreement with the measured data. As mentioned above, reaction 24 was studied by Vajo and co-workers<sup>11</sup> (see Eq. 2). Our calculated enthalpy of 50.4 kJ/mol H<sub>2</sub> overestimates the experimental value by  $\sim 10$  kJ/mol. However, since the experimental measurements were made at temperatures ( $T = 315$ – $400^\circ\text{C}$ ) above the LiBH<sub>4</sub> melting point ( $T_m = 268^\circ\text{C}$ ),<sup>6</sup> and our calculations are with respect to the ground state *Pnma* crystal structure,<sup>6</sup> we expect  $\Delta H^{\text{calc}}(\text{Pnma}) > \Delta H^{\text{expt}}(\text{liquid})$  due to the higher enthalpy of the liquid state.

We begin our discussion of the candidate reactions by commenting on the vibrational contributions ( $\Delta S_{\text{vib}}$ ) of the solid state phases to the total dehydrogenation entropy,  $\Delta S$ . Based on the notion that  $\Delta S$  is largely due to the entropy of H<sub>2</sub> [ $\Delta S \simeq S_0^{H_2} \simeq 130$  J/(mol K) at 300 K], a dehydrogenation enthalpy in the approximate range of 20–50 kJ/mol H<sub>2</sub> would yield desorption pressures/temperatures that are consistent with the operating conditions of a FC.<sup>3</sup> However, as shown in the last column of Table I, the calculated  $\Delta S_{\text{vib}}$  are not negligible (up to 21%) in comparison to  $S_0^{H_2}$ , calling into question the assumption  $\Delta S \simeq S_0^{H_2}$  and the guideline  $\Delta H = 20$ – $50$  kJ/mol H<sub>2</sub>. This suggests that a precise determination of the pressure-temperature characteristics of a given desorption reaction requires evaluating the change in Gibbs free energy [ $\Delta G(T)$ ], accounting explicitly for the effects of temperature and  $\Delta S_{\text{vib}}$ , as done below.

### A. Thermodynamic Guidelines

A key concern when attempting to predict favorable hydrogen storage reactions is to ensure that the thermodynamically preferred reaction pathway has been identified. This is a non-trivial task, and our experience has shown that intuition alone is not sufficient to correctly identify realistic reactions involving multicomponent systems.<sup>26</sup> In this regard, several of the reactions in Table I (denoted by \*) are noteworthy as they illustrate the difficulties that may arise when “guessing” at reactions. For example, all of the candidate reactions are written as simple, single-step reactions. While this may seem reasonable given the mechanism proposed in Ref. 11 (Eq. 2) and its generalization in Eq. 3, as we discuss below, some of these reactions should proceed via multiple step pathways, with each

TABLE I:  $H_2$  densities and calculated thermodynamic quantities for candidate  $H_2$  storage reactions. Units are J/K/mol  $H_2$  for  $\Delta S_{\text{vib}}$  and kJ/mol  $H_2$  for  $\Delta E$  and  $\Delta H$ ; column 7 refers to the temperature at which  $P_{H_2} = 1$  bar. Reactions denoted with a \* will not proceed as written (see text). The enthalpies of reactions 24–27 have been measured in prior experiments, and are included here (in parentheses) to validate the accuracy of our calculations. For comparison, system-level targets for gravimetric and volumetric density are cited in the bottom row.<sup>28</sup>

Rxn. No.	Reaction	Wt. % (kg $H_2$ /kg)	Vol. density (g $H_2$ /L)	$\Delta E$	$\Delta H^{T=300K}$	$T, P=1$ bar (°C)	$\Delta S_{\text{vib}}^{T=300K}$
1*	$4\text{LiBH}_4 + 2\text{AlH}_3 \rightarrow 2\text{AlB}_2 + 4\text{LiH} + 9\text{H}_2$	12.4	106	54.8	39.6	83	-18.4
2	$2\text{LiBH}_4 + \text{Al} \rightarrow \text{AlB}_2 + 2\text{LiH} + 3\text{H}_2$	8.6	80	77.0	57.9	277	-26.9
3*	$4\text{LiBH}_4 + \text{MgH}_2 \rightarrow \text{MgB}_4 + 4\text{LiH} + 7\text{H}_2$	12.4	9.5	68.2	51.8	206	-23.3
4*	$2\text{LiBH}_4 + \text{Mg} \rightarrow \text{MgB}_2 + 2\text{LiH} + 3\text{H}_2$	8.9	76	65.9	46.4	170	-29.4
5	$2\text{LiBH}_4 + \text{TiH}_2 \rightarrow \text{TiB}_2 + 2\text{LiH} + 4\text{H}_2$	8.6	103	21.4	4.5		-23.3
6	$2\text{LiBH}_4 + \text{VH}_2 \rightarrow \text{VB}_2 + 2\text{LiH} + 4\text{H}_2$	8.4	105	24.7	7.2	-238	-21.7
7	$2\text{LiBH}_4 + \text{ScH}_2 \rightarrow \text{ScB}_2 + 2\text{LiH} + 4\text{H}_2$	8.9	99	48.8	32.6	26	-21.4
8*	$2\text{LiBH}_4 + \text{CrH}_2 \rightarrow \text{CrB}_2 + 2\text{LiH} + 4\text{H}_2$	8.3	109	33.9	16.4	-135	-19.2
9*	$2\text{LiBH}_4 + 2\text{Fe} \rightarrow 2\text{FeB} + 2\text{LiH} + 3\text{H}_2$	3.9	76	32.7	12.8	-163	-24.6
10	$2\text{LiBH}_4 + 4\text{Fe} \rightarrow 2\text{Fe}_2\text{B} + 2\text{LiH} + 3\text{H}_2$	2.3	65	21.6	1.2		-24.4
11	$2\text{LiBH}_4 + \text{Cr} \rightarrow \text{CrB}_2 + 2\text{LiH} + 3\text{H}_2$	6.3	84	50.9	31.7	25	-23.8
12	$\text{Ca}(\text{BH}_4)_2 \rightarrow \frac{2}{3}\text{CaH}_2 + \frac{1}{3}\text{CaB}_6 + \frac{10}{3}\text{H}_2$	9.6	107	57.1	41.4	88	-16.0
13*	$\text{Ca}(\text{BH}_4)_2 + \text{MgH}_2 \rightarrow \text{CaH}_2 + \text{MgB}_2 + 4\text{H}_2$	8.4	99	61.6	47.0	135	-16.2
14*	$2\text{Ca}(\text{BH}_4)_2 + \text{MgH}_2 \rightarrow 2\text{CaH}_2 + \text{MgB}_4 + 7\text{H}_2$	8.5	98	63.6	47.9	147	-17.0
15*	$\text{Ca}(\text{BH}_4)_2 + \text{Mg} \rightarrow \text{CaH}_2 + \text{MgB}_2 + 3\text{H}_2$	6.4	79	60.6	41.9	111	-22.0
16*	$\text{Ca}(\text{BH}_4)_2 + \text{Al} \rightarrow \text{CaH}_2 + \text{AlB}_2 + 3\text{H}_2$	6.3	83	71.7	53.4	200	-19.5
17*	$\text{Ca}(\text{BH}_4)_2 + \text{AlH}_3 \rightarrow \text{CaH}_2 + \text{AlB}_2 + \frac{9}{2}\text{H}_2$	9.1	109	51.2	36.6	39	-13.5
18	$\text{Ca}(\text{BH}_4)_2 + \text{ScH}_2 \rightarrow \text{CaH}_2 + \text{ScB}_2 + 4\text{H}_2$	6.9	102	44.8	29.2	-20	-15.9
19	$\text{Ca}(\text{BH}_4)_2 + \text{TiH}_2 \rightarrow \text{CaH}_2 + \text{TiB}_2 + 4\text{H}_2$	6.7	106	17.4	1.1		-17.7
20	$\text{Ca}(\text{BH}_4)_2 + \text{VH}_2 \rightarrow \text{CaH}_2 + \text{VB}_2 + 4\text{H}_2$	6.6	108	20.8	3.8		-16.2
21*	$\text{Ca}(\text{BH}_4)_2 + \text{CrH}_2 \rightarrow \text{CaH}_2 + \text{CrB}_2 + 4\text{H}_2$	6.5	113	29.9	13.1	-180	-13.6
22	$\text{Ca}(\text{BH}_4)_2 + \text{Cr} \rightarrow \text{CaH}_2 + \text{CrB}_2 + 3\text{H}_2$	5.0	86	45.6	27.2	-38	-16.4
23	$6\text{LiBH}_4 + \text{CaH}_2 \rightarrow \text{CaB}_6 + 6\text{LiH} + 10\text{H}_2$	11.7	93	61.9 (63) <sup>a</sup>	45.4	146	-22.7
24	$2\text{LiBH}_4 + \text{MgH}_2 \rightarrow \text{MgB}_2 + 2\text{LiH} + 4\text{H}_2$	11.6	96	65.6	50.4 (41) <sup>b</sup>	186	-21.7
25	$2\text{LiBH}_4 \rightarrow 2\text{LiH} + 2\text{B} + 3\text{H}_2$	13.9	93	81.4	62.8 (67) <sup>b</sup>	322	-27.1
26	$\text{LiBH}_4 \rightarrow \text{Li} + \text{B} + 2\text{H}_2$	18.5	124	103.5	89.7 (95) <sup>c</sup>	485	-15.3
27	$\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$	7.7	109	64.5	62.3	195	1.3
U.S. DOE system-level targets (2010/2015)					(65.8–75.2) <sup>d</sup>		

<sup>a</sup>Ref. 13; <sup>b</sup>Ref. 11; <sup>c</sup>Ref. 29; <sup>d</sup>Ref. 12

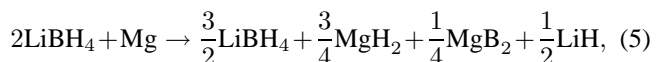
step having thermodynamic properties that are distinct from the presumed single-step pathway.

We group the examples of how chemical intuition might fail into three categories, and for each class, give a general guideline describing the thermodynamic restriction:

(1) *Reactant mixtures involving “weakly-bound” compounds:* We refer here to systems where the enthalpy to decompose one (or more) of the reactant phases is less than the enthalpy of the proposed destabilized reaction; thus, the weakly-bound phase(s) will decompose before (i.e., at a temperature below that which) the destabilized reaction can proceed. Two examples of this behavior can be found in Table I. The first case pertains to reactions 13–16, which, based on their larger enthalpies relative to reaction 12, would appear to “stabilize”  $\text{Ca}(\text{BH}_4)_2$ . In reality,  $\text{Ca}(\text{BH}_4)_2$  will decompose before (with  $P_{H_2} = 1$  bar at  $T = 88^\circ\text{C}$ ) any of the higher temperature reactions 13–16 will occur ( $T > 110^\circ\text{C}$ ), indicating that it is impossible to stabilize a reaction in this manner. Additional examples of this scenario occur in reactions 1, 8, 17, and 21, which involve the metastable  $\text{AlH}_3$  and  $\text{CrH}_2$  phases.

In the case of reaction 1,  $\text{AlH}_3$  will decompose first (yielding  $\text{Al}$  and  $\frac{3}{2}\text{H}_2$ ), followed by reaction of  $\text{Al}$  with  $\text{LiBH}_4$  (reaction 2). The consequences of this behavior are significant, since although the intended reaction 1 has an enthalpy ( $\sim 40$  kJ/mol  $H_2$ ) in the targeted range, in reality the reaction will consist of two steps, the first of which has an enthalpy below the targeted range ( $\text{AlH}_3$  decomposition), while the second (reaction 2) has an enthalpy above this range. *Guideline 1: The enthalpy of the proposed destabilized reaction must be less than the decomposition enthalpies of the individual reactant phases.*

(2) *Unstable combinations of product or reactant phases:* Reaction 4 illustrates how the seemingly straightforward process of identifying stable reactant and product phases can become unexpectedly complex. Here, the starting mixture of  $\text{LiBH}_4$  and  $\text{Mg}$  is unstable and will undergo the exothermic transformation:



which will consume the available  $\text{Mg}$  and form  $\text{MgH}_2$ , which

will itself react endothermically with the remaining  $\text{LiBH}_4$  according to reaction 24. The exothermic nature of Eq. (5) can be understood by noting that the enthalpy of reaction 4 (46.4 kJ/mol  $\text{H}_2$ ) is lower than the decomposition enthalpy of  $\text{MgH}_2$ , given by reaction 27 (62.3 kJ/mol  $\text{H}_2$ ). Therefore, the total energy can be lowered by transferring hydrogen to the more strongly bound  $\text{MgH}_2$  compound. *Guideline 2: If the proposed reaction involves a reactant that can absorb hydrogen (such as an elemental metal), the formation enthalpy of the corresponding hydride cannot be greater in magnitude than the enthalpy of the destabilized reaction.*

(3) *Lower-energy reaction pathways:* Reaction 3, involving a 4:1 mixture of  $\text{LiBH}_4\text{:MgH}_2$ , as well as the related reaction involving a 7:1 stoichiometry,  $7\text{LiBH}_4 + \text{MgH}_2 \rightarrow \text{MgB}_7 + 7\text{LiH} + 11.5\text{H}_2$ , were recently suggested in Ref. 13, which considered only a single-step mechanism resulting in the formation of  $\text{MgB}_4$  and  $\text{MgB}_7$ , respectively. Here we demonstrate that these reactions will not proceed as suggested there due to the presence of intermediate stages with lower energies. In fact, both hypothetical reactions have larger enthalpies [ $\Delta E = 69$  (4:1) and  $74$  (7:1) kJ/mol  $\text{H}_2$ <sup>13</sup>] than the 2:1 mixture (reaction 24), suggesting that, upon increasing temperature, the 4:1 and 7:1 mixtures will follow a pathway whose initial reaction step is the 2:1 reaction (reaction 24), which will consume all available  $\text{MgH}_2$ . Subsequent reactions between unreacted  $\text{LiBH}_4$  and newly-formed  $\text{MgB}_2$  will become thermodynamically feasible at temperatures above that of reaction 24, since their enthalpies exceed 50 kJ/mol  $\text{H}_2$ . [Similar behavior is expected for reactions 9 & 10, as the 1:1 mixture of  $\text{LiBH}_4\text{:Fe}$  (reaction 9) will initially react in a 1:2 ratio (reaction 10), which has a lower enthalpy.] *Guideline 3: In general, it is not possible to tune the thermodynamics of destabilized reactions by adjusting the molar fractions of the reactants. There is only one stoichiometry corresponding to a single-step reaction with the lowest possible enthalpy; all other stoichiometries will release  $\text{H}_2$  in multi-step reactions, where the initial reaction is given by the lowest-enthalpy reaction.*<sup>34</sup>

## B. Destabilized Reactions

In total, the preceding examples reveal that great care must be taken in predicting hydrogen storage reactions. Having ruled out the specious reactions, we now discuss the thermodynamics of the remaining reactions. Using the calculated thermodynamic data (Table I) as input to the van't Hoff equation,  $P_{\text{H}_2} = P_0 \exp(-\frac{\Delta G}{RT})$ , where  $P_0 = 1$  bar, Fig. 1 plots the equilibrium  $\text{H}_2$  desorption pressures of these reactions as a function of temperature.<sup>35</sup> Included in the plot is a rectangle delineating desirable temperature and pressure ranges for  $\text{H}_2$  storage:  $-40$ – $100^\circ\text{C}$ , and  $1$ – $700$  bar.

As expected, our van't Hoff plot confirms that the experimental reactions having large dehydrogenation enthalpies (reactions 24–27) yield pressures  $P \ll 1$  bar, even at elevated temperatures. On the other hand, some of the candidate reactions, for example 5 and 19, readily evolve  $\text{H}_2$  at very low temperatures (consistent with their low enthalpies) and are

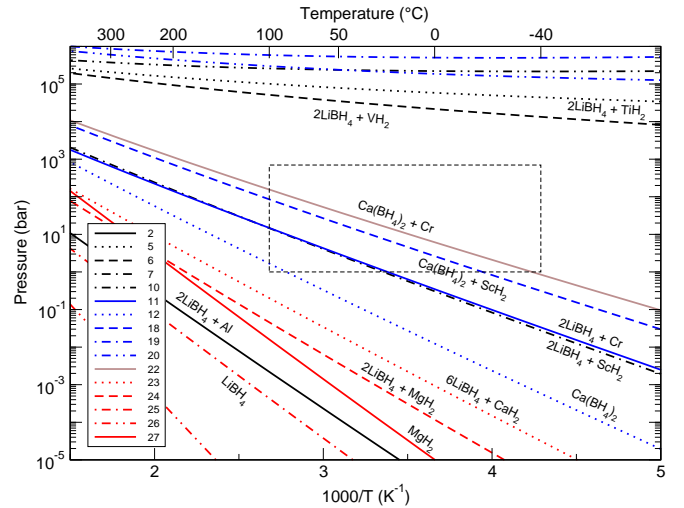


FIG. 1: (Color online) Calculated van't Hoff plot for reactions listed in Table I. The region within the dashed box corresponds to desirable temperatures and pressures for on-board hydrogen storage:  $P_{\text{H}_2} = 1$ – $700$  bar,  $T = -40$ – $100^\circ\text{C}$ .

therefore too weakly bound for practical, reversible on-board storage. However, the candidate reactions involving mixtures with  $\text{ScH}_2$ <sup>36</sup> (reactions 7<sup>37</sup> and 18) and  $\text{Cr}$  (reactions 11 and 22) desorb  $\text{H}_2$  in  $P$ - $T$  regimes that strongly intersect the window of desirable operating conditions. These reactions have room-temperature enthalpies in the range of 27–33 kJ/mol  $\text{H}_2$ , relatively high  $\text{H}_2$  densities (5–8.9 wt.%  $\text{H}_2$  and 85–100 g  $\text{H}_2/\text{L}$ ), and achieve  $P_{\text{H}_2} = 1$  bar at moderate temperatures ranging from 26 and  $-38^\circ\text{C}$ . Thus, via a first-principles approach of rapid screening through a large number of candidate reactions, and the careful use of thermodynamic considerations to eliminate unstable or multi-step reactions, we predict here several reactions with attributes that surpass the state-of-the-art for reversible, low-temperature storage materials.

## IV. CONCLUSION

In conclusion, using first-principles free energy calculations we have demonstrated that further significant destabilization of the strongly-bound  $\text{LiBH}_4$  and  $\text{Ca}(\text{BH}_4)_2$  borohydrides is possible, and we identify several high  $\text{H}_2$ -density reactions having thermodynamics compatible with the operating conditions of mobile  $\text{H}_2$ -storage applications. Unlike other recent predictions, the proposed reactions utilize only known compounds with established synthesis routes, and can therefore be subjected to immediate experimental testing. In addition, we provide guidance to subsequent efforts aimed at predicting new  $\text{H}_2$  storage materials by illustrating common pitfalls that arise when attempting to “guess” at reaction mechanisms, and by suggesting a set of thermodynamic guidelines to facilitate more robust predictions.

## Acknowledgments

V.O. thanks the U.S. DOE for financial support under grants DE-FG02-05ER46253 and DE-FC36-04GO14013.

- 
- \* Present address: Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208
- <sup>1</sup> F. E. Pinkerton and B. G. Wicke, *Industrial Physicist* **10**, 20 (2004).
  - <sup>2</sup> G. W. Crabtree, M. S. Dresselhaus, and M. V. Buchanan, *Physics Today* **57**, 39 (2004).
  - <sup>3</sup> L. Schlapbach and A. Züttel, *Nature* **414**, 353 (2001).
  - <sup>4</sup> G. Sandrock, *J. Alloys Compd.* **293-295**, 877 (1999).
  - <sup>5</sup> J.-P. Soulie, G. Renaudin, R. Cerny, and K. Yvon, *J. Alloys Compd.* **346**, 200 (2002).
  - <sup>6</sup> A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, P. Mauron, and C. Emmenegger, *J. Alloys Compd.* **356-357**, 515 (2003).
  - <sup>7</sup> Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S. Towata, A. Züttel, and S. Orimo, *Phys. Rev. B* **74**, 045126 (2006).
  - <sup>8</sup> Z. Łodziana and T. Vegge, *Phys. Rev. Lett.* **93**, 145501 (2004).
  - <sup>9</sup> K. Miwa, M. Aoki, T. Noritake, N. Ohba, Y. Nakamori, S. ichi Towata, A. Züttel, and S. ichi Orimo, *Phys. Rev. B* **74**, 155122 (2006).
  - <sup>10</sup> J. J. Reilly and R. H. Wiswall, *Inorganic Chem.* **7**, 2254 (1968).
  - <sup>11</sup> J. J. Vajo, S. L. Skeith, and F. Mertens, *J. Phys. Chem. B Lett.* **109**, 3719 (2005).
  - <sup>12</sup> F. D. Manchester, ed., *Phase Diagrams of Binary Hydrogen Alloys* (ASM, Materials Park, OH, 2000).
  - <sup>13</sup> S. V. Alapati, J. K. Johnson, and D. S. Sholl, *J. Phys. Chem. B* **110**, 8769 (2006).
  - <sup>14</sup> B. Bogdanović and M. Schwickardi, *J. Alloys Compd.* **253-254**, 1 (1997).
  - <sup>15</sup> W.-Q. Deng, X. Xu, and W. A. Goddard, *Phys. Rev. Lett.* **92**, 166103 (2004).
  - <sup>16</sup> Y. Zhao, Y.-H. Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang, *Phys. Rev. Lett.* **94**, 155504 (2005).
  - <sup>17</sup> T. Yildirim and S. Ciraci, *Phys. Rev. Lett.* **94**, 175501 (2005).
  - <sup>18</sup> H. Lee, W. I. Choi, and J. Ihm, *Phys. Rev. Lett.* **97**, 056104 (2006).
  - <sup>19</sup> Q. Sun, P. Jena, Q. Wang, and M. Marquez, *J. Am. Chem. Soc.* **128**, 9741 (2006).
  - <sup>20</sup> G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
  - <sup>21</sup> P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
  - <sup>22</sup> J. P. Perdew, J. A. Chevary, S. H. Vosko, et al., *Phys. Rev. B* **46**, 6671 (1992).
  - <sup>23</sup> D. C. Wallace, *Thermodynamics of Crystals* (John Wiley & Sons, 1972).
  - <sup>24</sup> S. Wei and M. Y. Chou, *Phys. Rev. Lett.* **69**, 2799 (1992).
  - <sup>25</sup> C. Wolverton, V. Ozoliņš, and M. Asta, *Phys. Rev. B* **69**, 144109 (2004).
  - <sup>26</sup> D. J. Siegel, C. Wolverton, and V. Ozoliņš, *Phys. Rev. B* **75**, 014101 (2007).
  - <sup>27</sup> C. Wolverton and V. Ozolins, *Phys. Rev. B* **75**, 064101 (2007).
  - <sup>28</sup> S. Satyapal, J. Petrovic, C. Read, G. Thomas, and G. Ordaz, *Catal. Today* **120**, 246 (2007).
  - <sup>29</sup> M. W. Chase, Jr., *NIST-JANAF Thermochemical Tables, 4th Edition* (American Chemical Society, 1998).
  - <sup>30</sup> A. Sudik, private communication.
  - <sup>31</sup> D. J. Siegel, V. Ozolins, and C. Wolverton, *Phys. Rev. B* p. in preparation (2007).
  - <sup>32</sup> S. V. Alapati, J. K. Johnson, and D. S. Sholl, *Phys. Chem. Chem. Phys.* **9**, 1438 (2007).
  - <sup>33</sup> Experimental testing of hydrogen storage materials—many of which are air-sensitive—can be a slow, painstaking process. For example, an equilibrium measurement of the extent of hydrogen desorption/uptake at a single temperature may require several *months* to complete in kinetically-hindered materials.<sup>30</sup> In contrast, the first-principles thermodynamic calculations presented here (encompassing more than 20 unique reactions) were completed in 2-3 weeks.
  - <sup>34</sup> This discussion assumes that the entropies of all competing reaction pathways are similar. Our results in Table I show that this is generally not the case; generalization of the above guidelines to the free energies is straightforward and will be presented elsewhere<sup>31</sup>.
  - <sup>35</sup> We neglect the LiBH<sub>4</sub> structural transition at  $T_s \sim 108^\circ\text{C}$ <sup>5</sup>, which should reduce the slope of the data in Fig. 1 for  $T > T_s$ .
  - <sup>36</sup> It should be noted that the high cost of Sc may preclude its use in practical applications.
  - <sup>37</sup> This reaction was also reported in Ref. 32